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Study of Uranium Solubility in Gallium–Indium Eutectic Alloy by emf Method[1]

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Abstract—Activity, activity coefficients and solubility of uranium in Ga–In eutectic alloy as well as activity of uranium in U–Ga and U–In alloys were determined between 573 and 1073 K using electromotive force (emf) method.

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Salt melts and metallic alloys exhibit high thermal and radiation stability and thus are prospective working media for developing pyroelectrochemical methods of reprocessing spent nuclear fuels (SNF) and practical realization of short closed nuclear fuel cycle. Liquid state of metals and salts at relatively low temperatures gives the simplest solution to one of the important tasks in radiochemical technology, the task of phase separation. It is obvious that detailed and reliable information concerning the behaviour of all SNF components, first of all uranium, in molten salt and liquid metal media is required for developing and improving pyroelectrochemical methods of SNF reprocessing. Existing literature [1] contains data on uranium behaviour in binary alloys with a number of low melting metals. Low melting metals can be effectively employed for separating (selective extraction) of SNF components in a liquid metal—molten salt system [2]. Alloys of low melting metals can be used instead of individual metals to lower melting point of the metallic phase and, thus, working temperature. However, we could not find information concerning the behaviour and thermodynamic properties of SNF components, particularly uranium, in ternary liquid metallic alloys. Ga–In eutectic alloy has one of the lowest melting points (T_{eut} = 288.7–289.0 K) and is liquid even at room temperature.

There is no information about the ternary Ga–In–U phase diagram. Of the corresponding binary systems only Ga–U alloys were studied in detail [5]. It appears that In–U phase diagram was not so far constructed. UMe_3 intermetallic compound (Me = Ga, In) is present in the equilibrium with the low melting component. In both systems this intermetallic compound forms cubic crystals of $AuCu_3$ type with close cell parameters [3].

The aim of the present work was experimental determination of uranium activity, activity coefficients and solubility in Ga–In eutectic based alloys between 573 and 1073 K.

For determining thermodynamic characteristics of uranium in liquid metallic alloys the emf of the following galvanic cell was measured:

$$(-)\ \mathrm{U}|\text{chloride melt} - \mathrm{UCl_3}|\mathrm{U} + \mathrm{Ga{-}In_{eut}}\ (+).$$

Low melting ternary LiCl–KCl–CsCl eutectic mixture (T_m = 536 K) was employed as a chloride melt for preparing working electrolytes. The individual alkali metal chlorides used for preparing the solvent salt were purified using the procedure described earlier [4]. Melts containing uranium(III) chloride were obtained by anodic dissolution of metallic uranium with chlorine electrode acting as a cathode. Uranium concentration in the electrolytes was 3–5 wt %. Ga–In alloys of the eutectic composition (21.8 wt % indium [5]) were prepared by fusing individual metals of 99.9999% (Ga) and 99.9995% (In) purity in an inert atmosphere dry box (MBraun Unilab 1200/780). Uranium containing alloys were obtained by adding metallic uranium or U–Ga alloy (containing ca. 5 wt % U) to the Ga–In eutectic or by cathodically depositing uranium on the liquid metal alloy directly in the experimental cell.

Electrochemical measurements were performed in the experimental cell schematically shown in Fig. 1. During the experiments the cell was filled with argon additionally purified by passing through heated zirconium turnings. The cell was loaded with the metals and uranium containing salt in the dry box. The cell was then closed, transferred to a vertical tube furnace

[1] The article was translated by the author.

and heated to 923–973 K. The electrode potentials were measured relative to metallic uranium at zero current employing an Autolab PGStat 302N potentiostat/galvanostat. The potential values were considered as equilibrium at a given temperature if they did not exhibit a tendency to a monotonic shift and changed by no more than 0.1–0.5 mV over an hour. Under these conditions the potentials of the alloys with the same phase composition were reproducible within ±0.1–0.2 mV. The measurements were performed over 573–1073 K temperature range. First stable emf readings after beginning the experiment were reached after 5–6 hours. After subsequent temperature change the equilibrium emf values were achieved in 1–3 hours. The melt temperature was measured employing a K-type thermocouple (Omega Engineering, Inc.) submerged into the melt in a beryllium oxide sheath, and a model 2751-K temperature recorder (Digitron Instrumentation, Ltd.).

A molybdenum rod acted as a current conductor to metallic uranium electrode and tungsten wire was used for liquid metal alloys. Thermal emf between molybdenum and tungsten in the temperature range employed in the present study is quite small and a corresponding correction (derived from the literature data [6]) was added to the experimental emf values. In the range of 280–1500 the thermal emf between molybdenum and tungsten can be described by the following expression:

$$\Delta E_{(\mathrm{Mo–W})} = 4.27 \times 10^{-6} \times T^2 - 7.88 \times 10^{-3} T + 1.84\ \mathrm{V}. \quad (1)$$

After completing the experiment the experimental cell was cooled and quenched salt was dissolved in cold distilled water. Uranium containing metallic alloys were then washed from the salts with water and ethanol, and dried at room temperature. For determining composition of the metallic alloys they were quantitatively dissolved in a mixture of hydrochloric and nitric acids; and the solution thus obtained was analysed by ICP-MS.

γ-Uranium and super-cooled liquid uranium were taken as standard states for determining uranium activity and activity coefficients in the studied systems. To account for uranium phase transformations the following correction was added to the experimental emf values:

$$\Delta E = -\left(\frac{RT}{nF}\right)\ln a_0, \quad (2)$$

where a_0 is uranium activity at a working temperature relative to γ-uranium or liquid uranium. The value of $\ln a_0$ was calculated from the known thermodynamic characteristics of uranium polymorphic transformations [7, 8]. For example, in case of α-U with γ-U taken as the standard state the activity was calculated in the following order:

$$R\ln a_0 = \frac{\Delta H_\alpha}{T_\alpha T}(T_\alpha - T) + \frac{\Delta H_\beta}{T_\beta T}(T_\beta - T), \quad (3)$$

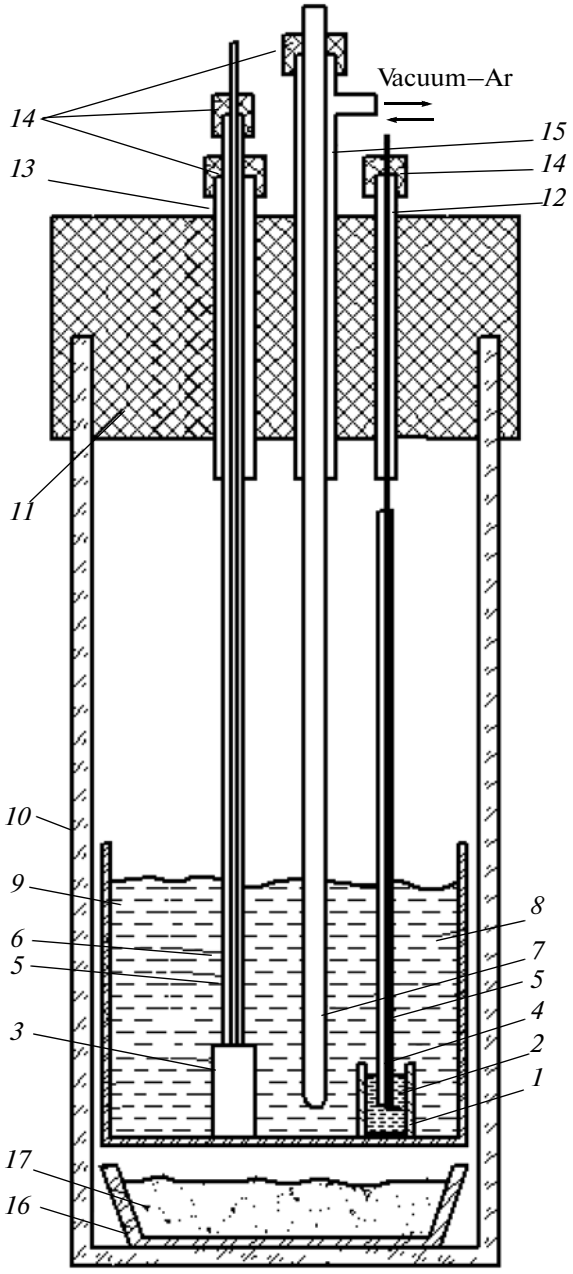

Fig. 1. Experimental cell for measuring emf of the galvanic cell. *1*—small beryllium oxide crucible; *2*—studied liquid alloy; *3*—metallic uranium (reference electrode); *4, 6*—current conductors; *5*—alumina ceramic tube; *7*—beryllium oxide thermocouple sheath; *8*—molten salt electrolyte; *9*—large beryllium oxide crucible; *10*—silica cell; *11*—rubber stopper; *12*, *13*, *15*—silica positioning tubes; *14*—rubber stoppers; *16*—alumina crucible; *17*—zirconium turnings (getter).

where ΔH_α and T_α are the heat and temperature of uranium $\alpha \rightarrow \beta$ transformation; and ΔH_β and T_β are the same parameters for the $\beta \rightarrow \gamma$ transformation.

Activity of uranium in liquid metal alloys was determined from the results of measuring emf of ura-

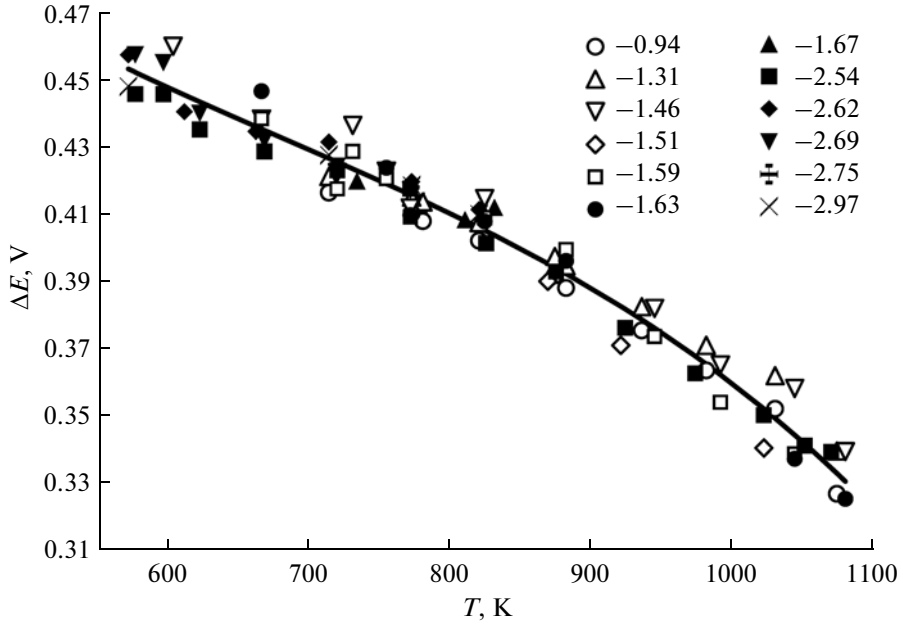

Fig. 2. The temperature dependence of emf of two-phase U–Ga–In alloys saturated with uranium measured vs. uranium metal. Logarithm of uranium concentration (molar fraction) in the alloys is given for each set of data.

nium saturated two-phase alloys. Activity coefficients were calculated using the results of emf measurements of dilute (homogeneous) alloys with known uranium content. Solubility of uranium in Ga–In eutectic based alloys was estimated from the difference of temperature dependencies of activity and activity coefficients.

The effect of temperature on emf of the two-phase U–Ga–In alloys is shown in Fig. 2. In the studied temperature range this dependence is non-linear and has an inflection around 900 K. Similar inflection was previously reported [9] for the temperature dependence of emf in U–Ga alloys around 920 K and explained by the existence of two modifications of UGa_3 intermetallic compound. Temperature dependencies of emf of two-phase Ga–In–U alloys at 569–1080 K calculated for two different uranium standard states are satisfactorily described by the following equations:

$$E_{\gamma\text{-U(Ga–In)}} = -2.87 \times 10^{-10} T^3 + 5.38 \times 10^{-7} T^2 - 5.45 \times 10^{-4} T + 0.653\ (\pm 0.012\ \text{V}), \quad (4)$$

$$E_{\text{l-U(Ga–In)}} = -3.34 \times 10^{-10} T^3 + 6.50 \times 10^{-7} T^2 - 6.54 \times 10^{-4} T + 0.706\ (\pm 0.012\ \text{V}). \quad (5)$$

Activity of γ-U and super-cooled liquid uranium in the Ga–In eutectic based alloys were calculated from the results of emf measurements. In the range of 569–1080 K the temperature dependencies of uranium activity are described by the following expressions:

$$\log a_{\gamma\text{-U(Ga–In)}} = 1.04 \times 10^6 T^{-2} - 1.19 \times 10^4 T^{-1} + 5.49(\pm 0.24), \quad (6)$$

$$\log a_{\text{l-U(Ga–In)}} = 1.04 \times 10^6 T^{-2} - 1.24 \times 10^4 T^{-1} + 5.81(\pm 0.24). \quad (7)$$

Comparison of the activity of γ-U in Ga–In–U alloys obtained in the present study with the literature data on binary Ga–U and In–U alloys (all original data were brought to γ-U as the standard state) is presented in Fig. 3. The figure shows that a_U in the Ga–In eutectic based alloys is considerably lower than in the alloys with indium and close to U activity in the alloys with gallium. The only exception is the data obtained by measuring Ga vapour pressure above the alloys with uranium [3], line *3* in Fig. 3. A possible reason for this, as pointed out by the authors themselves [13], is the presence in the gas phase of volatile gallium oxide together with gallium vapour. The literature contains data on uranium activity in the alloys with gallium or indium determined by emf method only at high temperatures, from 643 K for Ga and from 626 K for indium [9, 11–13]. It was therefore of interest to determine uranium activity in alloys with gallium and indium at lower temperatures, 573–1073 K. The results obtained here for γ-uranium (Fig. 3) agree very

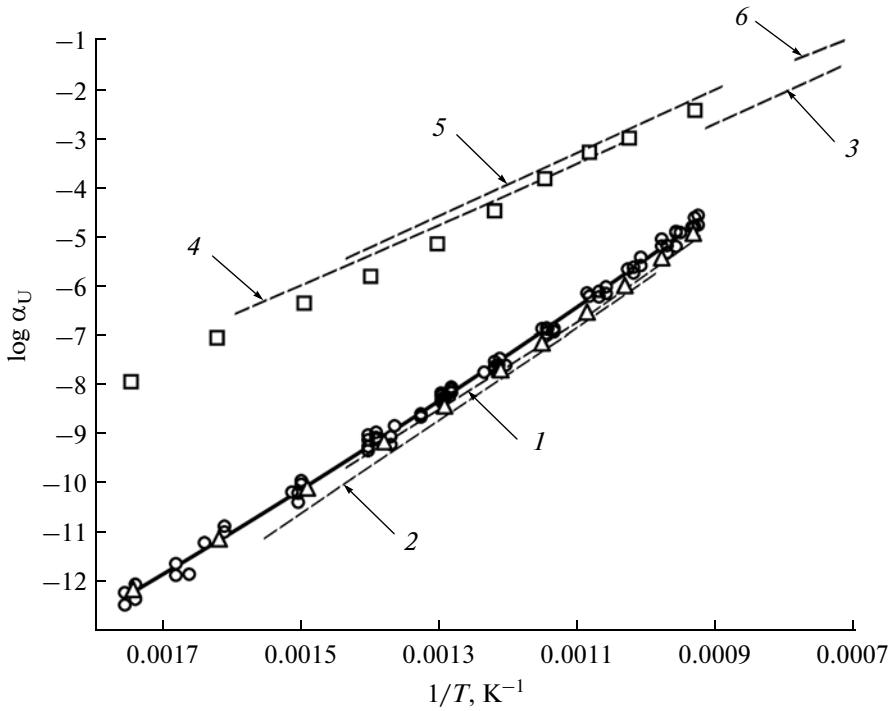

Fig. 3. Activity of γ-U in U–In, U–Ga and U–Ga–In systems. Symbols show the results obtained in the present work for the alloys based on Ga–In (○), Ga (△), In (□). Dashed lines show the literature data: *1* [12], *2* [9], *3* [13] for U–Ga, *4* [12], *5* [11], *6* [13] for U–In.

well with the literature data and are described by the following expressions:

$$\log a_{\gamma\text{-U(Ga)}} = 1.62 \times 10^6 T^{-2} - 1.31 \times 10^4 T^{-1} + 5.88(\pm 0.08), \quad (8)$$

$$\log a_{\gamma\text{-U(In)}} = 1.03 \times 10^6 T^{-2} - 9.64 \times 10^3 T^{-1} + 5.78(\pm 0.23). \quad (9)$$

It is worth noting that a_U in Ga–In–U liquid alloys is very close to uranium activity in Ga–U alloys and below 660 K they are essentially identical.

Activity coefficients of γ-U and super cooled liquid uranium in the alloys based on the Ga–In eutectic were determined from the results of emf measurements of dilute (homogeneous) Ga–In–U alloys. The temperature dependencies of uranium activity coefficients in Ga–In–U alloys in the studied temperature range of 574–1076 K are non-linear and can be satisfactorily described by the following equations:

$$\log \gamma_{\gamma\text{-U(Ga–In)}} = -1.91 \times 10^6 T^{-2} - 2.15 \times 10^3 T^{-1} + 1.42(\pm 0.67), \quad (10)$$

$$\log \gamma_{\text{l-U(Ga–In)}} = -1.84 \times 10^6 T^{-2} - 2.80 \times 10^3 T^{-1} + 1.89(\pm 0.67). \quad (11)$$

A comparison of γ_U in the alloys based on gallium, indium (from the existing literature data) and Ga–In eutectic mixture is presented in Fig. 4. Uranium activity coefficients in Ga–In–U alloys are close to those in Ga–U alloys and below 670 K they are even somewhat lower that could be expected for uranium-gallium system according to Lebedev et al. [9] but above those obtained by Johnson and Feder [12].

The temperature dependencies of uranium activity and activity coefficients obtained in the present work were used to calculate uranium solubility in Ga–In eutectic alloy at 573–1073 K and the following expression was obtained:

$$\log x_{\text{U(Ga–In)}} = 2.94 \times 10^6 T^{-2} - 9.79 \times 10^3 T^{-1} + 4.07. \quad (12)$$

The temperature dependence of x_U in Ga–In alloy is shown in Fig. 5. The solubility curve has an inflection at around 700 K and below that uranium solubility does not change much with temperature.

Figure 5 also shows the comparison of x_U in alloys based on the Ga–In eutectic with the literature data for the alloys based on gallium or indium. Above 740 K solubility of uranium in the Ga–In alloy lies between data for the alloys with Ga and In but below this temperature it starts deviating towards higher values. It is necessary to note that the set of data 2 in Fig. 5 (x_U in Ga Johnson and Chasanov [10] determined from the results of chemical analysis of equilibrium alloys after precipitating excessive intermetallic phases) at 693–772 agrees well with our results on uranium solubility

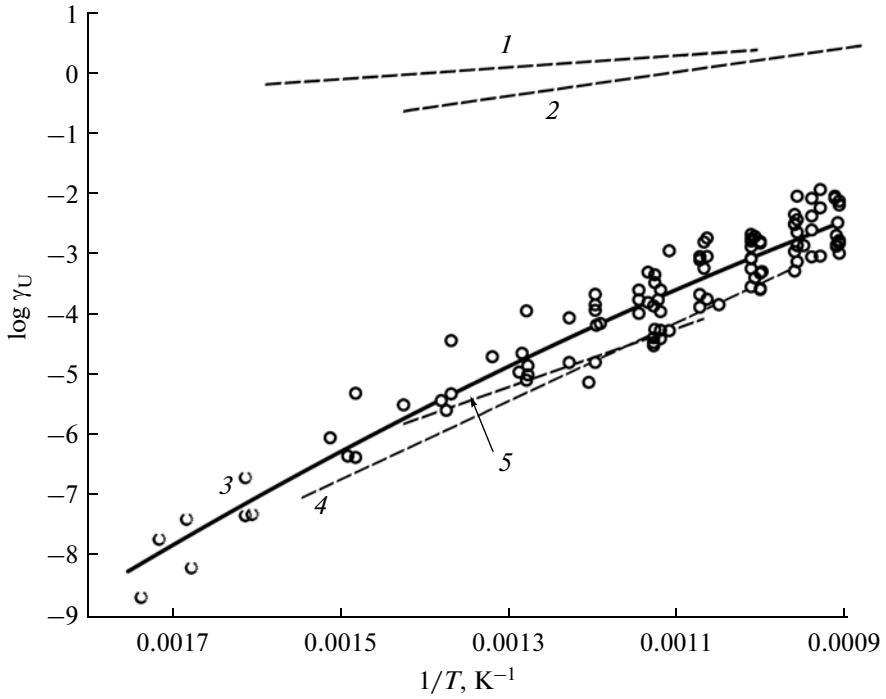

Fig. 4. Activity coefficients of γ-U in liquid alloys with indium (*1* [12], *2* [11]), Ga–In eutectic (*3*, present work), and gallium (*4* [12], *5* [9]).

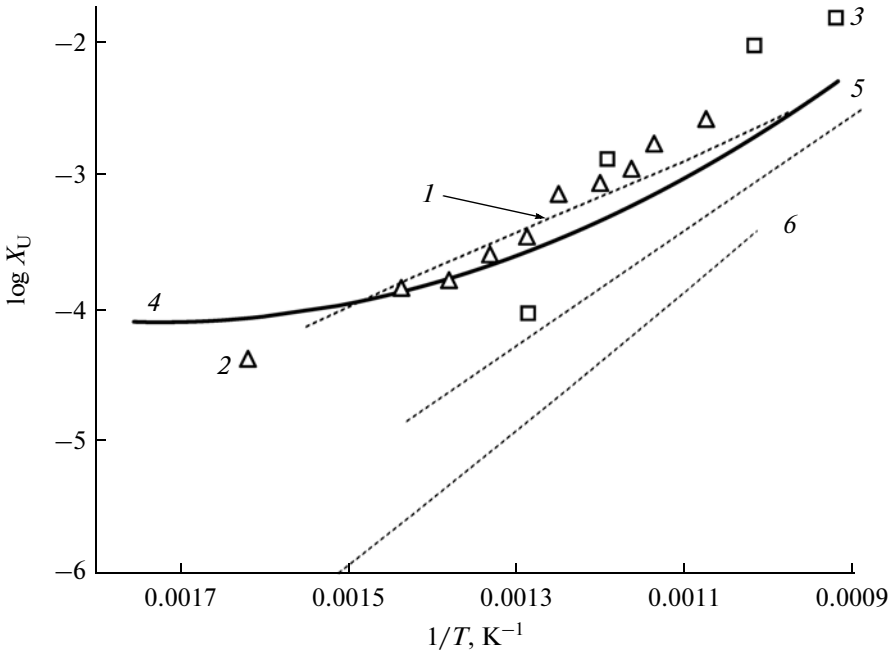

Fig. 5. Solubility of uranium in gallium (*1* (line) [12], *2* (symbols) [10], *3* (symbols) [15]), Ga–In eutectic (*4*, present work), indium (*5* [11], *6* [10, 12]).

in Ga–In system. Below 693 K Johnson and Chasanov [10] determined solubility only at 616 K and, as pointed out by Shank [14], it is likely that the obtained value did not correspond to the equilibrium state.

Thus, in the present work uranium activity, activity coefficients and solubility were determined for the first time in Ga–In eutectic alloys at 573–1073 K. Thermodynamic characteristics of binary uranium alloys with gallium and indium, obtained previously for a narrower temperature range, were refined.

REFERENCES

1. V. A. Lebedev, V. I. Kober, and L. F. Yamshchikov, *Thermochemistry of Alloys of Rare Earth and Actinide Elements* (Metallurgiya, Chelyabinsk, Chelyabinsk office, 1989), p. 336.
2. V. A. Lebedev, *Selectivity of Liquid Metal Electrodes in Fused Halides* (Metallurgiya, Chelyabinsk, Chelyabinsk office, 1993), p. 232.
3. *ASM Binary Phase Diagrams* (USA, ASM International, Software, 1996).
4. O. S. Ivanov, T. A. Badaeva, R. M. Sofronova, et al., *State Diagrams and Phase Transformations of Uranium Alloys* (Nauka, Moscow, 1972), p. 254.
5. V. A. Volkovich, D. A. Danilov, B. D. Vasin, and A. A. Khokhryakov, "Spectroscopic study of rhenium in alkali halide melts," Rasplavy, No. 4, 21–28 (2006).
6. N. L. Rogelberg and V. M. Beilin, *Thermocouple Alloys* (Metallurgiya, Moscow, 1983), p. 360.
7. *Thermal Constants of Compounds*, Vol. VIII, part 1: *Tables of accepted values*, Ed. by V. N. Glushko (AN SSSR, Moscow, 1978), p. 535.
8. *The Chemistry of the Actinide and Transactinide Elements*, Ed. by L. R. Morss, N. M. Edelstein, and J. Fuger (Springer, Dordrecht, 2010), Vol. 1, p. 698.
9. V. A. Lebedev, V. M. Seregin, A. M. Poyarkov, et al., "Thermodynamic properties of liquid alloys in uranium-gallium system," Zh. Fiz. Khim. **47** (3), 712–714 (1973).
10. J. R. Johnson and M. G. Chasanov, "Uranium solubility in liquid Ga, In, Tl and Pb," Trans. ASM **56**, 272–277 (1963).
11. V. A. Lebedev, V. M. Seregin, A. M. Poyarkov, et al., "Thermodynamic properties of liquid alloys in uranium-indium system," Zh. Fiz. Khim. **48** (3), 542–545 (1974).
12. I. Johnson and H. M. Feder, "Thermodynamics of binary systems of uranium with Zn, Cd, Ga, In, Tl, Sn, and Pb," in *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1962), pp. 319–331.
13. C. B. Alcock, J. B. Cornish, and P. Grieveson, "Knudsen effusion studies of compounds of uranium and thorium with elements of groups IIIb and IVb," in *Thermodynamics* (IAEA, Vienna, 1966), Vol. 1, pp. 211–230.
14. F. Shank, *Structures of Binary Alloys* (Metallurgiya, Moscow, 1973), p. 760.
15. W. D. Wilkinson, *Uranium Metallurgy*, Vol. 2: *Uranium Corrosion and Alloys* (Interscience Publishers, New York, 1962), p. 734.